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# Elastic constants of III–V compound semiconductors: modification of Keyes' relation

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**Abstract.** We have proposed new empirical relations between elastic constants and lattice constants for III–V compound semiconductors with the zincblende (ZB) structure by modifying Keyes' relation. The new relations show excellent agreement with available experimental data and give considerably better estimates than do the extended Hückel tight-binding method and the bond-orbital model. We have calculated the elastic constants for AlP, BAs, AlN, GaN and InN with the ZB structure using the relations. For III nitrides the elastic constants in the wurtzite phase have also been calculated combining the relations and Martin's formula. The values so obtained are reasonable but less reliable than those for the ZB phase.

## 1. Introduction

The elastic properties of most III–V compound semiconductors have been extensively studied and clarified. However, for some materials which are difficult to grow as single crystals and epitaxial films of good quality, the elastic constants have not been determined experimentally. It is necessary to calculate the elastic constants quantitatively for such materials.

Kitamura and co-workers [1, 2] and Shen [3] have calculated the elastic properties of 30 materials with the diamond and zincblende (ZB) structures using the extended Hückel tight-binding (XHTB) method and the bond-orbital model (BOM), respectively. For seven semiconductors with the ZB structure, *ab initio* calculations have also been performed to obtain the elastic stiffness constants by some research groups [4–8]. Keyes [9] has proposed a simple empirical relation for the elastic constants of materials with the diamond, ZB and wurtzite (WZ) structures. However, it cannot explain recent experimental results for BN [10] and BP [11].

In this paper we have proposed new relations, a modified version of Keyes' empirical relation, which hold for III–V compound semiconductors with the ZB structure including BN and BP. The values of elastic constants for AlP, BAs, AlN, GaN and InN have been obtained using them. We have also given the elastic constants for III nitrides in the WZ phase using the proposed relations and Martin's [12] formula [13] and have compared them with previous theoretical and experimental results.

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## 2. Elastic constants of III–V compound semiconductors with the zincblende structure

Most III–V compound semiconductors crystallize in the ZB structure. Keyes [9] has proposed an empirical relation between the elastic constants of materials with the diamond, ZB and WZ structures based on dimensional analysis. The relation for III–V compound semiconductors with the ZB structure is summarized as follows: the reduced elastic constants $C_{11}^*$, $C_{12}^*$, and $C_{44}^*$ are almost independent of material, and $C_{ij}^* = C_{ij}/C_0$ where $C_{ij}$ are the elastic stiffness constants and $C_0 = e^2/b^4$ with the electronic charge $e$ and the nearest-neighbour distance $b$.

**Table 1.** Experimental elastic constants and lattice constants of III–V compound semiconductors with the ZB structure. The values in parentheses are the densities.

| Material | Elastic constant ($10^{11}$ dyn cm$^{-2}$) $C_{11}$ | $C_{12}$ | $C_{44}$ | Lattice constant (Å) (Density (g cm$^{-3}$)) | Reference |
|---|---|---|---|---|---|
| BN | 82.0 | 19.0 | 48.0 | 3.618[a] (3.480) | [10] |
| BP | 31.5 | 10 | 16 | 4.5383[b] | [11] |
| GaP | 14.05 | 6.203 | 7.033 | 5.451[a] (4.1297) | [15] |
| InP | 10.11 | 5.61 | 4.56 | 5.873[a] (4.780) | [16] |
| AlAs | 11.99 | 5.75 | 5.66 | 5.661 72 | [17] |
| GaAs | 11.90 | 5.38 | 5.95 | 5.653 25 | [18] |
| InAs | 8.329 | 4.526 | 3.959 | 6.058 38[c] | [19] |
| AlSb | 8.769 | 4.341 | 4.076 | 6.1355 | [21] |
| GaSb | 8.834 | 4.023 | 4.322 | 6.094[a] (5.619) | [22] |
| InSb | 6.669 | 3.645 | 3.020 | 6.479[a] (5.7751) | [23] |

[a] These values are calculated from the density and atomic masses.
[b] [14].
[c] [20].

In table 1 we summarize the experimental elastic constants and lattice constants of III–V compound semiconductors with the ZB structure. It should be pointed out that the elastic constants for BN and BP are large compared with those for the other materials.

Figure 1 shows the reduced elastic constants which are calculated using the values listed in table 1. If Keyes' relation holds, $C_{11}^*$, $C_{12}^*$ and $C_{44}^*$ should be independent of the lattice constant. Except for BN and BP, the relation seems to hold approximately. For materials with lattice constants smaller than about 5 Å, however, Keyes' relation cannot explain the experimental data. As the lattice constant increases, $C_{11}^*$ and $C_{44}^*$ tend to decrease monotonically, while $C_{12}^*$ tends to increase monotonically. Therefore, Keyes' relation should be modified.

We have simply extended Keyes' relation for III–V compound semiconductors whose bonding properties are partly ionic and partly covalent and have found that the following new relations can explain the dependence of the reduced elastic constants on the lattice constants (shown in figure 1 by the broken lines):

$$C_{11}^* = 1.333 + 2.998/a \tag{1a}$$

$$C_{12}^* = 0.1521a \tag{1b}$$

$$C_{44}^* = 0.012\,35a + 0.1609 + 3.777/a \tag{1c}$$

where $a$ is the lattice constant in ångströms. The coefficients in the above equations have been determined by the least-squares method.

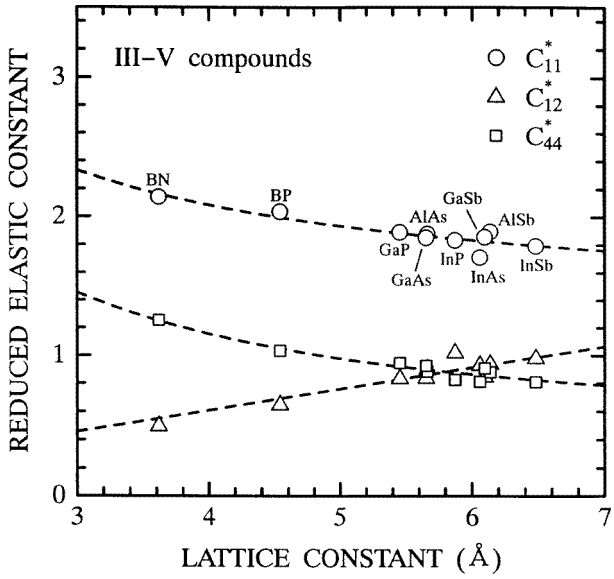


**Figure 1.** Reduced elastic constants versus lattice constants for III–V compound semiconductors with the ZB structure: ○ , $C_{11}^*$; △, $C_{12}^*$; □, $C_{44}^*$. For explanation of broken lines, see text.

Equations (1*a*)–(1*c*) mean that the elastic constants can be expressed using three kinds of term which are proportional to $b^{-3}$, $b^{-4}$ and $b^{-5}$, respectively, where $b$ is the distance between nearest-neighbour atoms. Although bulk moduli for alkali halide crystals with the rocksalt structure have been empirically found to have an approximately $b^{-3}$-dependence [24] and bulk moduli for semiconductors with the diamond structure have a $b^{-5}$-dependence within the BOM [25] in which potentials between the second-neighbour and more distant neighbour atoms are neglected, elastic constants are influenced in a complicated manner by various kinds of potential. So it is not easy to clarify the physical background of each term in the relations.

In table 2 are shown the elastic constants calculated using equations (1*a*)–(1*c*) for materials for which experimental data exist. For comparison, the results of previous calculations and experiments are also presented. For the XHTB method and the BOM, the values of $C_{11}$ and $C_{12}$ are calculated using the following relations:

$$C_{11} = B + \tfrac{4}{3}C_s \tag{2a}$$

$$C_{12} = B - \tfrac{2}{3}C_s \tag{2b}$$

where $B = (C_{11} + 2C_{12})/3$ is the bulk modulus and $C_s = (C_{11} - C_{12})/2$ is the elastic shear constant.

In figure 2, plots of the calculated elastic constants versus experimental values are shown. It is clear that our results are nearly on the straight broken lines which represent agreement between calculated and experimental values. For almost all the materials the results obtained by the XHTB method and the BOM agree less well than ours with the experimental values especially for BN and BP. Our calculations give better results than do the *ab initio* calculations in some cases.

Using the new relations, we have also calculated the elastic constants for several materials which have not been determined experimentally so far. Table 3 shows the

**Table 2.** Elastic constants calculated for III–V compound semiconductors with the ZB structure using the new empirical relations. For comparison, previous theoretical and experimental results are also shown.

| | Elastic constant ($10^{11}$ dyn cm$^{-2}$) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{11}$ | | | | | $C_{12}$ | | | | | $C_{44}$ | | | | |
| Material | XHTB[a] | BOM[b] | *Ab initio* | This work | Exp.[c] | XHTB[a] | BOM[b] | *Ab initio* | This work | Exp.[c] | XHTB[a] | BOM[b] | *Ab initio* | This work | Exp.[c] |
| BN | 56.6 | 121 | 84.4[d] | 82.8 | 82.0 | 23.6 | 50.5 | 19[d] | 21.1 | 19.0 | 20.2 | 49.5 | 48.3[d] | 47.9 | 48.0 |
| BP | 35.4 | 42.6 | 35.9[d] | 30.8 | 31.5 | 7.03 | 17.6 | 8.1[d] | 10.7 | 10 | 14.4 | 17.5 | 20.2[d] | 16.2 | 16 |
| GaP | 12.9 | 14.5 | 14.7[e] | 14.0 | 14.05 | 5.78 | 6.18 | 6.1[e] | 6.16 | 6.203 | 5.56 | 5.89 | 7.9[e] | 6.85 | 7.033 |
| InP | 8.76 | 9.45 | | 10.2 | 10.11 | 4.74 | 4.11 | | 4.93 | 5.61 | 3.75 | 3.80 | | 4.84 | 4.56 |
| AlAs | 12.4 | 12.9 | 11.6[f] | 11.9 | 11.99 | 4.89 | 5.52 | 5.5[f] | 5.50 | 5.75 | 5.14 | 5.23 | 5.7[f] | 5.73 | 5.66 |
| GaAs | 11.6 | 12.5 | 12.3[g] | 12.0 | 11.90 | 5.07 | 5.30 | 5.3[g] | 5.52 | 5.38 | 5.29 | 5.07 | 6.2[g] | 5.78 | 5.95 |
| InAs | 8.51 | 8.08 | | 8.90 | 8.329 | 4.19 | 3.52 | | 4.49 | 4.526 | 3.73 | 3.25 | | 4.19 | 3.959 |
| AlSb | 9.89 | 9.18 | | 8.44 | 8.769 | 3.17 | 3.88 | | 4.32 | 4.341 | 4.30 | 3.74 | | 3.95 | 4.076 |
| GaSb | 9.91 | 8.94 | | 8.68 | 8.834 | 3.35 | 3.76 | | 4.41 | 4.023 | 4.52 | 3.65 | | 4.07 | 4.322 |
| InSb | 7.25 | 5.91 | | 6.69 | 6.669 | 2.97 | 2.53 | | 3.67 | 3.645 | 3.35 | 2.40 | | 3.07 | 3.020 |

[a] [1, 2].
[b] [3].
[c] References are listed in table 1.
[d] [8].
[e] [6].
[f] [5].
[g] [4].

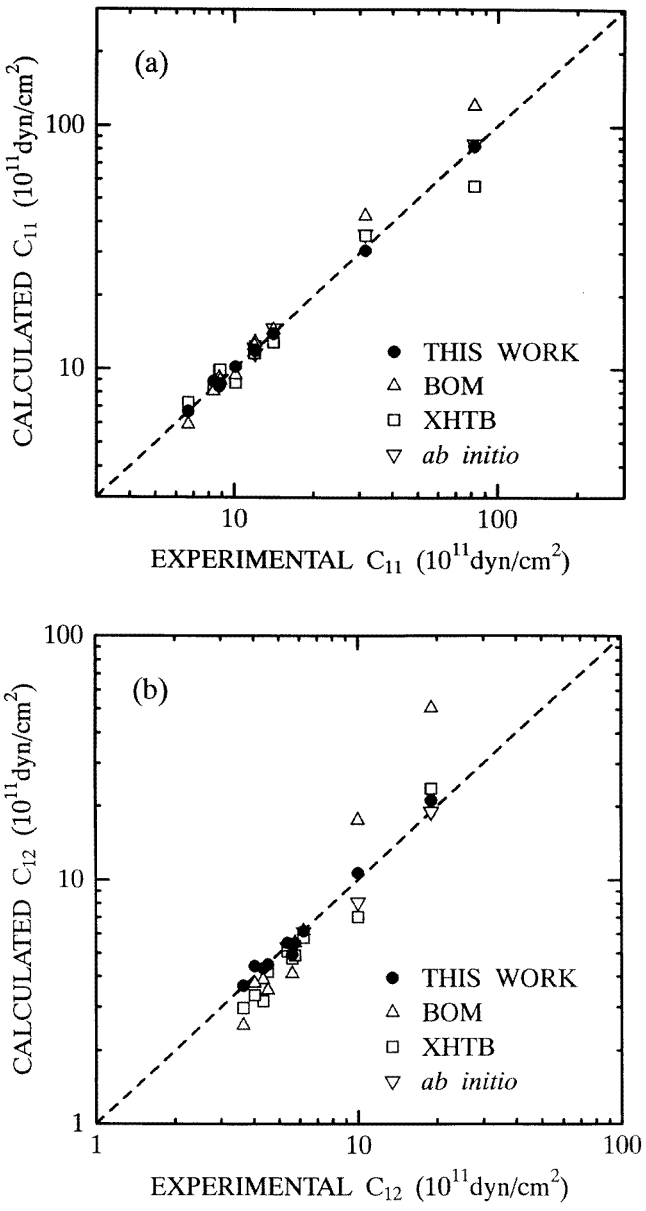


**Figure 2.** Calculated elastic constants (*a*) $C_{11}$, (*b*) $C_{12}$ and (*c*) $C_{44}$ versus experimental values for III–V compound semiconductors with the ZB structure: ●, this work; △, the BOM [3]; □, the XHTB method [1, 2]; ▽, *ab initio* calculations [4–6, 8]; – – –, agreement between calculated and experimental values. For the correspondences of the plots to materials, see table 2.

elastic constants calculated for AlP, BAs, AlN, GaN and InN with the ZB structure. For comparison, the available results from *ab initio* calculations are also shown in parentheses. Although AlN, GaN and InN crystallize in the WZ structure at equilibrium, epitaxial films in the ZB phase can be obtained under suitable conditions. For AlP there is good agreement between our calculations and the *ab initio* values; for GaN there are some discrepancies.

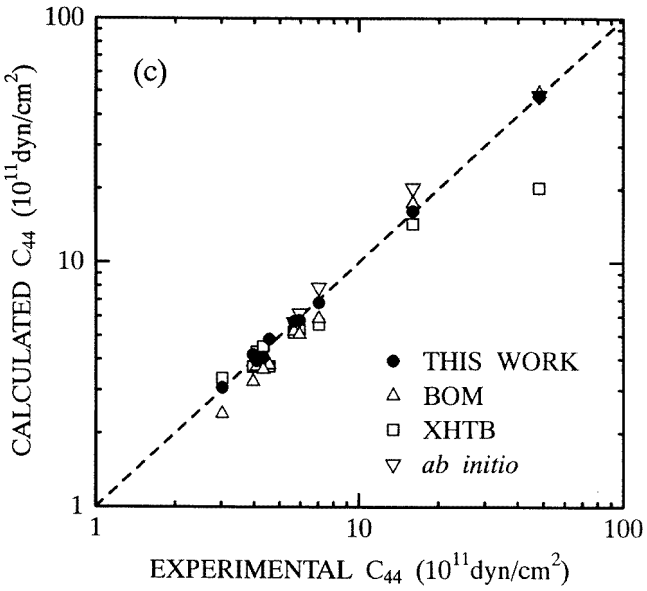


**Figure 2.** (Continued)

It is desirable to determine the values experimentally, using good-quality films which have become available recently.

**Table 3.** Elastic constants calculated for III–V compound semiconductors with the ZB structure by the new empirical relations using the lattice constants shown in the fifth column. Results of *ab initio* calculations are also presented in parentheses.

| Material | Elastic constant ($10^{11}$ dyn cm$^{-2}$) $C_{11}$ | $C_{12}$ | $C_{44}$ | Lattice constant (Å) | Reference |
|---|---|---|---|---|---|
| AlP | 13.9 | 6.12 | 6.77 | 5.4635[a] | This work |
| | (13.4) | (6.8) | (7.0) | (5.40) | [6] |
| BAs | 24.7 | 9.16 | 12.7 | 4.777[b] | This work |
| AlN | 36.0 | 11.9 | 19.2 | 4.38[c] | This work |
| GaN | 31.4 | 10.8 | 16.5 | 4.52[d] | This work |
| | (29.6) | (15.4) | (20.6) | (4.46) | [7] |
| InN | 20.6 | 8.08 | 10.5 | 4.98[e] | This work |

[a] [26].
[b] [27].
[c] [28].
[d] [29].
[e] [30].

## 3. Elastic constants of III nitrides in the wurtzite phase

As is mentioned above, AlN, GaN and InN crystallize in the WZ structure at equilibrium. As for BN, the ZB phase is stable and the WZ phase is metastable.

Martin [12] has derived an approximate transformation of elastic constants from the ZB phase to the WZ phase and vice versa, based on a simple model in which the following is assumed: all interactions between the third-neighbour and more distant neighbour atoms can be neglected; the WZ structure is ideal, i.e. $c/a = 1.633$ where $c/a$ is the ratio of lattice constants; the difference between the ZB and WZ structures is only the rotation of neighbouring tetrahedra. Using the transformation, Sherwin and Drummond [13] have calculated the elastic constants of ZB AlN, GaN and InN from available experimental data in the WZ phase [31, 32], and Kim *et al* [7] have transformed the elastic constants of ZB GaN, which were obtained by *ab initio* calculations, into those of WZ GaN.

We transform the elastic constants of nitrides in the ZB phase obtained by the new empirical relations into those in the WZ phase using Martin's formula. The results are shown in table 4. For comparison, the experimental data, which were obtained by the x-ray diffraction method for BN, GaN and InN and by Brillouin spectroscopy for AlN, are also presented in parentheses. Values of $C_{66}$ can be obtained using the relation $C_{66} = (C_{11} - C_{12})/2$.

**Table 4.** Elastic constants of III nitrides in the WZ phase transformed from those in the ZB phase using Martin's formula. Experimental data, which were obtained by Brillouin spectroscopy for AlN and by the x-ray diffraction method for the others, are shown in parentheses. The values in angular brackets are the results of *ab initio* calculations and are obtained from those in the ZB phase using Martin's transformation.

| | Elastic constant ($10^{11}$ dyn cm$^{-2}$) | | | | | |
|---|---|---|---|---|---|---|
| Material | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | Reference |
| BN | 98.1 | 17.2 | 9.73 | 106 | 35.0 | This work |
| | (52.0) | (43.1) | (37.0) | (42.4) | (6.5) | [31] |
| AlN | 42.4 | 10.3 | 7.13 | 45.5 | 13.8 | This work |
| | (41.05) | (14.85) | (9.89) | (38.85) | (12.46) | [33] |
| GaN | 36.9 | 9.42 | 6.67 | 39.7 | 11.8 | This work |
| | (29.6) | (13.0) | (15.8) | (26.7) | (2.41) | [31] |
| | ⟨39.6⟩ | ⟨14.4⟩ | ⟨6.4⟩ | ⟨47.6⟩ | ⟨9.1⟩ | [7] |
| InN | 24.3 | 7.19 | 5.25 | 26.3 | 7.23 | This work |
| | (19.0) | (10.4) | (12.1) | (18.2) | (0.99) | [31] |

First of all, we discuss the elastic constants of AlN because they were measured by Brillouin spectroscopy which is a reliable method for obtaining elastic constants. There are some discrepancies between our calculations and the experiments. The discrepancies could be caused by the considerable deviation in $c/a$ of 1.601 for AlN [29] from 1.633 and other approximations in Martin's model.

As for BN there are serious discrepancies between our calculated values and the experimental data. As is shown in section 2, our calculations for BN in the ZB phase are in excellent agreement with the experimental data. Our calculations for WZ BN should be valid within Martin's formula. Even if the corrections for Martin's model are taken into account, the discrepancies seem to be too large. Kim *et al* [7] have indicated that results obtained by the x-ray diffraction method may include considerable error. For this reason, the elastic constants of BN, GaN and InN in the WZ phase should be experimentally re-examined. For GaN, see below. We believe that our calculated values for BN, GaN and InN are more accurate than the available experimental data. The accuracy is expected to be better than that for AlN, since experimental values of $c/a$ are 1.654 [34], 1.626 [29] and 1.623 [29] for BN, GaN and InN, respectively.

In angular brackets in table 4 we also present the results of *ab initio* calculations for WZ GaN by Kim *et al* [7]. On comparison of them with our results, there are some discrepancies. Since the values were transformed from those in the ZB phase by Martin's formula, the discrepancies are attributed to the differences between the elastic constants in the ZB phase. Quite recently, Yamaguchi *et al* [35] have measured the Brillouin spectra of a high-quality WZ GaN epitaxial film of 4 $\mu$m thickness on a sapphire substrate and have determined the elastic constants of WZ GaN. The results are in good agreement with our calculations; for $C_{11}$, $C_{33}$, and $C_{44}$, the discrepancies are within 9%.

## 4. Summary

We have proposed new empirical relations between the elastic constants and lattice constants for III–V compound semiconductors with the ZB structure by modifying Keyes' relation. The relations reproduce available experimental data excellently. We have calculated the elastic constants of AlP, BAs, AlN, GaN and InN with the ZB structure using the relations. For III nitrides the elastic constants in the WZ phase have also been calculated using Martin's formula. We have made it possible to estimate the elastic constants for III–V compound semiconductors systematically.

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